

lative care, ensured exactitude for purposes of comparison between the behaviour of the magnetised and unmagnetised steel bars in the corrosive fluid.

An average of the twenty-nine experiments in Table I indicates an increase of corrosion in the steel due to magnetic influence of about 3 per cent. under the conditions of experimentation.

The steel bars were not highly magnetised, and I purposely exposed them to the action of the solution for somewhat long periods in the present experiments, as thereby, perhaps, affording a better indication of the influence of magnetisation on general corrosion, the almost immediate effect of magnetisation on the corrosion of steel having been demonstrated in the electrical observations of Part II.

It is probable that the deviation in the individual results of Table I, in the extent of the loss by corrosion, may be attributed to variation in the extent to which the several bars were magnetised. The results recorded in the present paper indicate that magnetisation exerts an effect, though small, on the extent of the corrosive action of copper salts on iron and steel. This is probably owing to the local currents, set up by magnetisation between the polar and central portions of the bars, inducing somewhat greater chemical action.

In some of the experiments with the copper solution which contained the more highly magnetised bars, the copper solution was of a perceptibly lighter colour towards the end of an experiment when compared with the colour of the copper solution containing the unmagnetised steel bar.

VIII. "Note on the Spectra of the Flames of some Metallic Compounds." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, LL.D., F.R.S., Jacksonian Professor, University of Cambridge. Received June 3, 1892.

[PLATE 5.]

A study of the spectra of flames offers many points of interest. It is long since A. Mitscherlich (Poggendorff's 'Annalen,' vol. 116, p. 499; vol. 121, p. 459) showed that the spectra of flames are, for the most part, those of compounds of the elements present, and contain comparatively few rays proceeding directly from the elements themselves. But there are many questions still undecided. For example, it is not known whether the vibrations which give the spectra of compounds in flames are those which the molecules of the compounds in question would assume under the action of a high temperature alone, or whether they are not vibrations of a different order, arising during

chemical changes, and deriving their energy directly from the chemical energy of the interacting substances. When the absorption spectrum of a compound is observed to correspond with its emission spectrum in a flame, we may infer that the vibrations are those which the compound molecule assumes when sufficiently heated. But there are not many cases in which this has been observed. We have observed it in the case of cyanogen ('Roy. Soc. Proc.,' vol. 44, p. 247, note), but we are not certain of any other case. The difference between the spectrum of the base of a flame and that of the upper part, observed in many flames, lends support to the supposition that there are rays which originate in the chemical change, perhaps occurring in the molecules which are in intermediate stages of the change, and not assumed by the molecules which are the final product, even when intensely heated in the upper part of the flame. The fact that the same rays which are seen in the base of a flame may be sometimes generated by electric discharges in the gases which are burnt in the flame, or in their products of combustion, is not at all inconsistent with this supposition, for such discharges certainly have electrolytic effects, and may very well give rise to molecules in the intermediate stages between one state of chemical combination and another.* The flames of substances, such as the organo-metallic compounds, into which metals enter as chemical ingredients, have not hitherto, so far as we know, been observed, and it is to two such flames that these notes refer.

Spectrum of the Flame of Nickel-Carbonyl.

The remarkable compound of nickel and carbonic oxide, $\text{Ni}(\text{CO})_4$, discovered by Mr. Mond, burns in air with a luminous, smoky flame, and the spectrum it emits appears to be a continuous one. When the vapour is burnt in oxygen instead of in atmospheric air, the spectrum still appears to be quite continuous; in fact, such a spectrum as carbonic oxide, without any nickel, gives under similar circumstances. This, however, is only in appearance, because the brightness of the continuous spectrum overpowers the feebler bands and lines which belong to the flame of the nickel compound. These bands and lines come out when the vapour of the nickel compound is diluted with a

* It is sometimes assumed in books on chemistry that the atoms which form a chemical compound can never be in an intermediate state between complete separation and complete combination. So inconceivable an assumption would hardly have been made except to support a theory, but it has nevertheless obtained a certain currency. It is supported by no fact and no analogy. Two atoms which are within the spheres of each other's influence, but have not yet reached the state of relative tranquillity which we recognise as chemical combination, may very conceivably be the seat of very violent agitation and vibratory motions, which cease when they are actually combined.

good deal of hydrogen. We have employed two methods of making such a mixture. The first was by passing a stream of dry hydrogen, mixed with carbonic oxide, over reduced nickel in a glass tube, and burning the issuing gas in a double jet with oxygen either outside or inside the burning gas. The nickel was freshly reduced at a gentle heat with hydrogen, and allowed to cool in carbonic oxide. When quite cold the stream of mixed hydrogen and carbonic oxide was found to take up quite enough nickel at the temperature of the room, and would continue to do so for some hours. After a time, however, the nickel required to be again warmed in a current of hydrogen, when some water was given off, and the metal recovered its sensitiveness. Another plan was to pass a stream of hydrogen through a U-tube containing a little of the liquid nickel compound in the bend. The result was the same in each case, but the proportion of vapour of the compound was more easily varied (by simply varying the proportion of carbonic oxide in the stream of gas) in the former method. The mixed gas and vapour burnt in air with a smoky flame, but in a full supply of oxygen with a bright yellowish-green flame without visible smoke. The first jet we used was of platinum, but nickel-carbonyl deposits nickel at a red heat, so that the platinum soon became coated with a thick deposit of nickel, which choked the orifices. This nickel adhered so closely to the platinum that it could not well be removed mechanically, and had to be dissolved off. We found it, therefore, more convenient to use a jet made of a piece of porcelain tube, about 1 cm. in diameter, with a narrow porcelain tube, fitted by means of a cork, in the axis of the wider tube. The mixed gas and vapour were passed either through the inner or through the outer tube, and oxygen through the other. The porcelain being a bad conductor, no nickel was deposited on it, except close to the orifice, whence it could be easily removed mechanically without disturbing the apparatus. The porcelain, of course, added some lines to the spectrum, but these were easily detected. In fact, we noticed only the lines of sodium, calcium, and lithium.

The spectrum of the flame of the nickel-carbonyl thus diluted consists of two parts: (1) the spectrum of the main body of the green flame, (2) that of the base of the flame when the oxygen is outside, and of the surface of the small inner cone when the oxygen is inside, the flame.

The spectrum of the main body of the flame consists of a series of shaded bands, brightest in the green, but extending on the red side beyond the red line of lithium, and on the violet side well into the blue, though with rapidly diminishing distinctness. These bands have their sharp bright edges on the more refrangible side, that is, they are turned in the opposite direction to the bands produced by electric

discharges in carbonic oxide at low pressure. The positions of the bright edges of the bands in the flame of the nickel-carbonyl have some correspondence with those of the bands produced by electric discharges in carbonic oxide, but it is not a very close one, and may be only accidental. With the dispersion employed, which gives a difference of deviation of $2^{\circ} 52'$ between D and F, there was no sign of a resolution of these bands into lines. The brightest bands had, however, their more refrangible edges pretty sharply defined, while the less bright bands, especially those in the blue, were very hazy. A certain amount of continuous spectrum, of course, overlay the bands, and made them somewhat less distinct. Photographs show that this continuous spectrum continues as far as $\lambda 3500$, but fading sensibly from $\lambda 4200$ onwards. The photographs do not show any extension of the bands beyond the blue.

Besides the bands, a few lines, but only a few, in the visible part of the spectrum, extend into the upper part of the flame. Of these few only one is a known line of nickel; it is the green line $\lambda 5476$. This was also the only line of nickel which we observed in the visible part of the spectrum in explosions of hydrogen and oxygen in a nickel-lined tube ('Roy. Soc. Proc.,' vol. 36, p. 475).

In the ultra-violet part of the spectrum of the flame a great number of nickel lines were photographed; indeed, by far the greater part of the lines of nickel found by us in the arc ('Phil. Trans.,' vol. 179 (1888), A, p. 247) between $\lambda 3972$ and $\lambda 2943\cdot5$. In this case also there is a close correspondence between the spectra of the flame and of the explosions, except that the lines of the flame are much more numerous than those recorded of the explosions. This difference, however, is probably due to the much shorter exposure of the photographs of explosions. Although the photographs show lines as high as $\lambda 2943$, the lines in this region are very faint, and gradually die out in proceeding from the less to the more refrangible side of the spectrum. In the region about L, M, and N the lines are very strong, so that it is for rays of those rates of vibration that nickel is most sensitive at the temperature of the flame.

Turning now to the base of the flame, we find a great number of lines, of which most extend but a short distance from the bottom of the flame. They form two principal groups, one in the orange and red, and the other in the citron and yellow. These lines are for the most partly sharply defined, and in the more refrangible parts of each group very fine and closely set. They are probably channellings following Rydberg's law, and somewhat confused by overlapping. The diagram indicates the strongest of these lines, as they appear on the background of shaded bands in the flame. It is drawn to a scale of oscillation frequencies.

None of these lines appear to be nickel lines, and, as they are limited

to the base of the flame, they cannot be ascribed to any of the final products of the combustion, such as nickel oxide, but must be due either to the as yet unaltered molecules of nickel carbonyl, or to some molecules intermediate between that compound and the products of combustion which have only a transitory existence, and may perhaps have a transitory agitation of a particular kind imparted to them by the chemical energy which changes its form in the combustion.

The following tables give the approximate oscillation frequencies of the edges of the principal shaded bands, and of the lines seen at the base of the flame, but the numbers are only approximate.

Oscillation Frequencies of Edges of Shaded Bands.

1496	1692	1933	2146
1521	1752	1960	2172
1577	1808	2052	2199
1594	1849	2107	2226
1635			

Oscillation Frequencies of Lines in the Base of the Flame.

1497	1582	1622	1721
1506	group of very closely set lines	1627 <i>l</i>	1727 <i>l</i>
1509		1631 <i>l</i>	1732 <i>l</i>
1514	1586	1651	1735
1518	1593	1656	1738
1521	1595	1663	1741 <i>l</i>
1526	1596	1667	1742
1543	1598	1671	1745
1547	1599	1673	1746
1549	1600	1682	1747
1555	1602	1686	1753
1560	1604	1690 <i>l</i>	1806
1563	1607	1706	1809
1572	1612	1712	1827
1575	1615	1714	1833
1578	1616	1716	1879
1580	1618		

The six numbers in the above table to which an *l* is added correspond to lines which extend into the upper part of the flame.

Table of Wave-lengths of Nickel Lines photographed from the
Flame.

2943·5	3183·8	3390·4	3561·1
2981·2	3194·9	3392·4	3565·7
2983·6	3196·6	3409·0	3571·2
2992·2	3201·5	3413·4	3587·2
2994·1	3221·1	3413·8	3601·4
3002·1	3224·6	3423·1	3609·8
3003·2	3226·3	3433·0	3612·1
3011·5	3232·6	3436·7	3618·8
3018·8	3234·2	3445·7	3624·1
3031·4	3242·6	3452·3	3663·4
3037·5	3247·8	3457·8	3669·7
3044·5	3250·1	3461·1	3673·4
3050·4	3270·6	3466·8	3687·6
3053·9	3282·2	3468·9	3694·6
3057·2	3285·0	3470·8	3721·6
3064·2	3315·1	3483·1	3736·1
*3080·3 ?	3319·7	3485·2	3737·0
3096·6	3321·6	3492·3	3745·0
3098·6	3361·0	3500·0	3775·0
3101·1 } 3101·4 }	3365·5 3367·2	3509·7 3514·4	3783·0 3791·0
3105·0	3368·9	3519·1	3806·6
3113·7	3371·3	3523·9	3831·7
3133·6	3373·6	3527·1	3857·8
3145·5	3380·0	3547·5	3972·0

The more refrangible lines in the foregoing table were very faintly depicted on the photographic plate, and it is possible that a more lengthened exposure than the fifteen minutes, which we employed in the region where the lines were faint, would have brought out more lines. The continuous spectrum of the limelight extends some distance further than the most refrangible of these nickel lines.

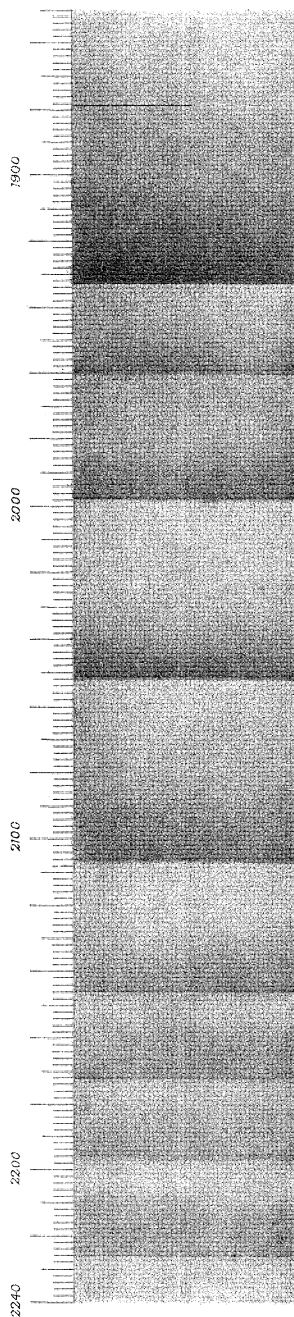
Flame of Zinc Ethide.

Zinc ethide burning undiluted produces so much continuous spectrum as to overpower any special rays. But by passing a stream of hydrogen through a bent tube containing zinc ethide, and burning the mixed gas and vapour in oxygen, as we did the nickel-carbonyl,

* A query is placed against this number because the water spectrum is so strong at this point that we cannot certainly distinguish the nickel line. There is no other reason for doubting its presence.

Spectrum of flame of Ni (CO)⁴ + H burning in Oxygen.

Scale of Oscillation frequencies.



we reduced the continuous spectrum sufficiently to enable us to observe any fairly strong rays which might be peculiar to the flame. In the visible part of the spectrum the three well-known rays of zinc in the blue λ 4812, 4721, and 4681 were easily seen. Photographs of the more refrangible part of the spectrum showed no trace of the ultra-violet lines of zinc; no more, in fact, than the flames of hydrocarbons usually show. Nor did there appear to be any rays from the base of the flame other than those seen in hydrocarbon flames in general. In our observations on explosions (*loc. cit.*) we did not find that a zinc lining to the tube in which the oxy-hydrogen gas was exploded brought out any zinc line, either in the visible or ultra-violet part of the spectrum. The flame of the compound containing zinc chemically combined may be supposed to give the rays of zinc more readily than the exploding gases, which merely take up the metal mechanically. But the flame does not, in either case, seem hot enough to develop the ultra-violet rays, though these are very strongly developed in the arc.

IX. "Preliminary Note on the Pressure developed by some New Explosives." By Captain NOBLE, C.B., F.R.S. Received June 10, 1892.

For a considerable time I have, with the assistance of Sir F. Abel and Professor Dewar, been engaged in researches upon the new explosives which during the last few years have attracted so much attention, and which apparently are destined to do much in developing the power of modern artillery.

From the nature of these researches and the considerable scale upon which they have to be conducted, as well as from certain difficulties which have manifested themselves, I am not at present in a position to submit to the Royal Society the results of these experiments; but, as one particular portion throws light upon a question of considerable importance, I propose very shortly to give the results at which I have arrived, leaving fuller details for a subsequent communication.

Artillerists of all nations are pretty well agreed that, save under exceptional circumstances, the maximum working pressure in a gun should not exceed 17 tons per square inch or, say 2500 atmospheres. The reasons for this limitation are weighty, but I need not here discuss them. Now, taking cordite and pebble powder as illustrations, since we can, even in guns not designed to fire the former explosive, obtain with the same maximum pressure, energies higher than those obtained with pebble powder by nearly 50 per cent., it is obvious that

Spectrum of flame of $\text{Ni}(\text{CO})_4 + \text{H}$ burning in Oxygen.

Scale of Oscillation frequencies.

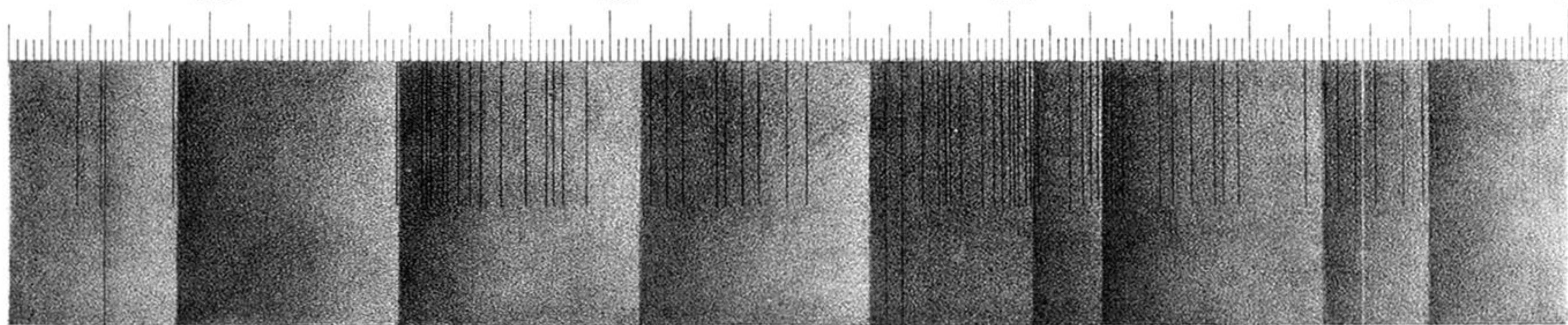
1800

1700

1600

1500

1460



Ni

2240

2200

2100

2000

1900

